

NOTES

INVESTIGATIONS IN THE FIELD OF SYNTHETIC DYES

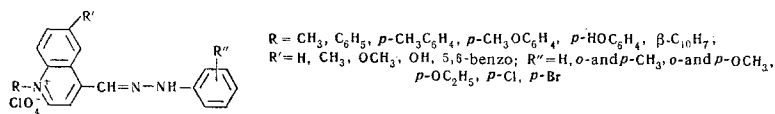
LXXVI. Synthesis of Arylhydrazones of N-Aryllepidinium Salts

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 2, p. 283, 1970

UDC 547.831+542.953+543.422+546.171.5

The results are given of a study of the condensation of quaternary salts of lepidine with diazoamino compounds, leading to the formation of arylhydrazones of the following type:



The direction of the reaction does not depend on the method of its performance or on the nature of the substituents R, R', and R''. Electron-donating substituents in the quaternary salt and electron-accepting substituents in the diazoamino compound slow down the reaction and decrease the yields of arylhydrazones. The hydrazone structure of the reaction products was confirmed by their IR spectra from the presence of a medium-intensity band at 3250–3220 cm⁻¹ belonging to the stretching vibrations of a N–H bond.

The absorption spectra in the visible region of the arylhydrazones obtained in ethanolic and ethanolic alkaline solutions have been studied. To explain the color changes as a function of the nature of the substituents introduced, the actual structure of the arylhydrazones is represented as an intermediate between two limiting structures, one being a structure with a positive charge on the heterocyclic nitrogen atom, which predominates in the ground state, and the other a structure with the charge on the nitrogen atom of the imino group, which predominates in the excited state. The nature of the substituents R, R', and R'', affecting the ratio of these structures, leads to color changes of the arylhydrazones. Methyl, methoxyl, and benzo groups in the quinoline nucleus have little effect on the color, while hydroxyl derivatives absorb at higher frequencies than the corresponding unsubstituted derivatives. Electron-accepting bromine atoms in the quinoline nuclei cause a bathochromic effect of 13 nm. Electron-donating substituents in the aryl nucleus of the hydrazone residue also have a bathochromic effect, and electron-accepting substituents have a hypsochromic effect, substituents in the ortho position having a weaker effect than those in the para position.

14 March 1966

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